ЖЭТФ, 2016, том 149, вып. 2, стр. 439–444

EXACT RESULTS ON DIFFUSION IN A PIECEWISE LINEAR POTENTIAL WITH A TIME-DEPENDENT SINK

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Received August 31, 2015

The Smoluchowski equation with a time-dependent sink term is solved exactly. In this method, knowing the probability distribution $P(0,s)$ at the origin, allows deriving the probability distribution $P(x,s)$ at all positions. Exact solutions of the Smoluchowski equation are also provided in different cases where the sink term has linear, constant, inverse, and exponential variation in time.

DOI: 10.7868/S0044451016020218

1. INTRODUCTION

The diffusion process of a particle in a potential having a sink is studied through the solution of the Smoluchowski equation [1]. It is of much interest to many scientists in chemical dynamics because it serves as a reference model for a wide variety of dynamical processes. A huge number of attempts has been made to study this diffusion process with a suitable position of the sink [2–4], in view of numerous applications in diffusion controlled reactions [5]. Such a model was used in [6,7] to calculate the rate of diffusion-controlled reactions as well as cyclization of polymer chains in solutions. In [8–10], such a model was used for electron transfer reactions in polar solvents. Recently, a diffusion equation with a sink term was used in [11] to develop a theory of uni-molecular reactions in clusters. Pressure influence on isomerization reactions is also explained in [12] using such a type of model. In [13, 14], a model of this kind was used to analyze barrierless electron relaxation in solution. Exact analytic results for diffusion problems helps in understanding the different parameters like friction and provide an insight into different approximations. Most of these works had focussed on the time evolution/propagator derivation in the case of one or more Dirac delta-function sinks with a constant strength in time.

There has been a huge amount of work on the analytic solution of the Smoluchowski equation in the context of various problems that do not involve any kind of time dependence; in other words, there are no cases where the Smoluchowski equation with a time-dependent sink is solved by analytic methods. No analytic solution is available even in the simplest possible case of a free particle. There is a large number of works on diffusion with a time-independent sink [15]. By contrast, this paper is devoted to the concept that deals mainly with a Dirac delta sink whose strength varies with time, and we are the first to consider this effect explicitly. There are two common methods for solving this problem. One is using a path integral method of the Feynman type and the other is using Laplace transforms. We use the latter method, although the two methods are closely related. Our method closely follows the method used for solving the Schrödinger wave equation. First-order rate constant can also be calculated by using the probability distribution function.

2. FORMULATION OF THE PROBLEM

We solve the Smoluchowski equation with a time-dependent sink for the problem shown in the Figure.

The simplest piecewise linear potential U can be represented by the equation

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial P(x,t)}{\partial x} + P(x,t)\frac{\partial U(x)}{\partial x}\right], \quad (1)$$

where D is a diffusion coefficient and P is a probability distribution.

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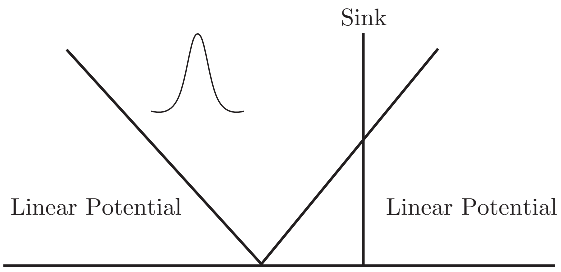

Schematic diagram showing the formulation of our problem

In our case, we consider

$$U(x) = \omega|x|,$$
$$U(x) = \begin{cases} -x\omega, & -\infty \le x \le 0, \\ x\omega, & 0 \le x \le \infty, \end{cases} \quad (2)$$

where ω is a constant.

In view of Eq. (2), Eq. (1) can be written as

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial P(x,t)}{\partial x} + P(x,t)\omega\right]. \quad (3)$$

Taking the Laplace transform of above equation yields

$$S\overline{P}(x,s) - P(x,0) = = D\left[\frac{\partial^2}{\partial x^2}\overline{P}(x,s) + \omega\frac{\partial}{\partial x}\overline{P}(x,s)\right], \quad (4)$$

which can be further rewritten as

$$-D\frac{\partial^2}{\partial x^2}\overline{P}(x,s) - \omega\frac{\partial}{\partial x}\overline{P}(x,s) + + S\overline{P}(x,s) = P(x,0),$$
$$\left[-D\frac{\partial^2}{\partial x^2} - \omega\frac{\partial}{\partial x} + S\right]\overline{P}(x,s) = P(x,0). \quad (5)$$

Integrating Eq. (5) from $x_0 - \epsilon$ to $x_0 + \epsilon$ and using the notation $p^2 = q^2 + S/D$, $S = D(p^2 - q^2)$, and $q = \omega/2$, we can write the general solution [16, 17] of the above equation in the two regions of interest as

$$\overline{P}(x,s) = a(s)\exp\left[-(p+q)|x|\right] + \frac{1}{2D(p+q)} \times \times \int\limits_{-\infty}^{\infty} \exp\left[-(p+q)|x-x_0|\right] P(x_0)\, dx_0. \quad (6)$$

The above equation determines the probability distribution at all positions. In what follows, we determine the variation of the sink in different cases.

3. INTRODUCING A TIME-DEPENDENT SINK TERM INTO THE SMOLUCHOWSKI EQUATION AND ITS EXACT SOLUTION

We consider the case with linear potential U represented by Eq. (2). The Smoluchowski equation with a time-dependent sink term can be written as

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial P(x,t)}{\partial x} + P(x,t)\left(\frac{\partial U}{\partial x}\right)\right] + + 2k(t)\delta(x)P(x,t). \quad (7)$$

For $0 \le x \le \infty$ and $-\infty \le x \le \infty$, the Smoluchowski equation can be written as

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2}P(x,t) + \omega D\frac{\partial}{\partial x}P(x,t) + + 2k(t)\delta(x)P(x,t), \quad x > 0, \quad (8)$$

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2}P(x,t) - \omega D\frac{\partial}{\partial x}P(x,t) + + 2k(t)\delta(x)P(x,t), \quad x < 0. \quad (9)$$

We now solve Eqs. (8), (9), but we must consider the homogeneous equations in order to satisfy the boundary conditions at the origin, i. e.,

$$\begin{aligned} \frac{\partial P(x,t)}{\partial t} &= D\frac{\partial^2}{\partial x^2}P(x,t) + \omega D\frac{\partial}{\partial x}P(x,t), \\ \frac{\partial P(x,t)}{\partial t} &= D\frac{\partial^2}{\partial x^2}P(x,t) - \omega D\frac{\partial}{\partial x}P(x,t). \end{aligned} \quad (10)$$

The solution of both these equations for all x, positive and negative, is given by Eq. (6).

Next, to determine the constant $a(s)$, we consider the Laplace transform of Eqs. (8), (9) which can be written as

$$S\overline{P}(x,s) - P(x,0) = D\frac{\partial^2}{\partial x^2}\overline{P}(x,s) + \omega D\frac{\partial}{\partial x}\overline{P}(x,s) + + 2\delta(x)L\left[k(t)P(x,t)\right], \quad (11)$$

where L is the Laplace transform. Integrating this from $x = 0 - \epsilon$ to $0 + \epsilon$, we have

$$\left[\frac{\partial}{\partial x}\overline{P}(x,s) + \omega\overline{P}(x,s)\right]_{0-\epsilon}^{0+\epsilon} + + \frac{2}{D}L\left[k(t)P(0,t)\right] = 0. \quad (12)$$

The last equation can again be rewritten as

$$\left[\frac{\partial\overline{P}(x,s)}{\partial x}\right]_{0-\epsilon}^{0+\epsilon} + 2\omega\overline{P}(0,s) + + \frac{2}{D}L\left[k(t)P(0,t)\right] = 0. \quad (13)$$

Further, the above equation can be simplified to

$$a(s)\,(p+q-\omega) = \frac{L}{D}\,[k(t)P(0,t)] - \\ - \frac{\omega}{2D}\int dx_0 \exp\left[(p+q)x_0\right] P(x_0). \quad (14)$$

With $P(x_0) = \delta(x - x_0)$, the above equation can be further rewritten as

$$a(s) = \frac{L\,[k(t)P(0,t)]}{D\,(p+q-\omega)} - \\ - \frac{\omega}{2D\,(p+q-\omega)\,(p+q)} \exp\left[(p+q)|x_0|\right]. \quad (15)$$

Using this value of the constant $a(s)$ in (6) help us in determining the probability distribution for a time-dependent sink:

$$\overline{P}(x,s) = \frac{L\,[k(t)P(0,t)]}{D\,(p+q-\omega)} \exp\left[(p+q)|x|\right] - \\ - \frac{\omega}{2D\,(p+q-\omega)\,(p+q)} \exp\left[(p+q)|x+x_0|\right] + \\ + \frac{1}{2D(p+q)} \int\limits_{-\infty}^{\infty} \exp\left[(p+q)|x-x_0|\right] P(x_0)\, dx_0, \quad (16)$$

which finally becomes

$$\overline{P}(x,s) = \frac{L\,[k(t)P(0,t)]}{D\,(p+q-\omega)} \exp\left[(p+q)|x|\right] - \\ - \frac{\omega}{2D\,(p+q-\omega)\,(p+q)} \exp\left[(p+q)|x+x_0|\right] + \\ + \frac{1}{2D(p+q)} \exp\left[(p+q)|x_0|\right]. \quad (17)$$

4. DETERMINATION OF THE PROBABILITY DISTRIBUTION $P(x,t)$, THE CONSTANT $a(s)$ WITH A TIME-DEPENDENT SINK TERM $k(t) = \alpha_0$

In this case, we assume that $k(t) = \alpha_0$, and hence the sink term can be written as

$$L\,[k(t)P(0,t)] = \int\limits_0^{\infty} e^{-st} \alpha_0 P(0,t)\, dt = \alpha_0 \overline{P}(0,s). \quad (18)$$

The constant $a(s)$ becomes

$$a(s) = \frac{\alpha_0 \overline{P}(0,s)}{D\,(p+q-\omega)} - \\ - \frac{\omega}{2D\,(p+q-\omega)\,(p+q)} \exp\left[(p+q)|x_0|\right]. \quad (19)$$

Putting this value of $a(s)$ in Eq. (6), we obtain

$$\overline{P}(x,s) = \frac{\alpha_0 \overline{P}(0,s) \exp[(p+q)|x|]}{D\,(p+q-\omega)} - \\ - \frac{\omega \exp[(p+q)|x+x_0|]}{2D\,(p+q-\omega)\,(p+q)} + \\ + \frac{\exp[(p+q)|x-x_0|]}{2D(p+q)}. \quad (20)$$

Setting $x = 0$ here, we find

$$\overline{P}(0,s) = \exp[(p+q)|x_0|] \times \\ \times \frac{-2\omega + p + q}{2(p+q)(p+q-\omega-\alpha_0)}. \quad (21)$$

With this value of $\overline{P}(0,s)$ substituted back in Eq. (20), after some simplification, we obtain the probability distribution function as

$$\overline{P}(x,s) = \frac{\exp[(p+q)|x+x_0|]}{2D(p+q-\omega)(p+q)} \times \\ \times \left[\frac{(p+q-\omega)\alpha_0}{D(p+q-\omega-\alpha_0)} - \omega\right] + \\ + \frac{\exp[(p+q)|x-x_0|]}{2D(p+q)}. \quad (22)$$

5. SOLUTION OF THE SMOLUCHOWSKI EQUATION WITH A TIME DEPENDENT SINK TERM $k(t) = -\alpha t$

In this case, we assume that $k(t) = -\alpha t$, and hence the sink term can be written as

$$L\,[k(t)P(0,t)] = L\,[-\alpha t P(0,t)] = \\ = \int\limits_0^{\infty} e^{-st} - \alpha t P(0,t)\, dt = \alpha \frac{\partial}{\partial s} \overline{P}(0,s). \quad (23)$$

We follow the same strategy as in Sec. 3 and arrive at equation Eq. (13).

We hence will find the value of $a(s)$ as

$$a(s) = \frac{1}{D(p+q)} \alpha \frac{\partial}{\partial s} \overline{P}(0,s) + \frac{\omega}{p+q} \overline{P}(0,s). \quad (24)$$

With this value of $a(s)$ in Eq. (6), we obtain the probability distribution function as

$$\overline{P}(x,s) = \frac{1}{D(p+q)} \alpha \frac{\partial}{\partial s} \overline{P}(0,s) \exp[-(p+q)|x|] + \\ + \frac{\omega}{p+q} \overline{P}(0,s) \exp[(p+q)|x|] + \\ + \frac{1}{2D(p+q)} \exp[-(p+q)|x-x_0|]. \quad (25)$$

Setting $x = 0$ in the above equation, and after simplification, we arrive at the equation

$$\frac{\partial}{\partial s}\overline{P}(0,s) - \left(\frac{pD}{\alpha} - \frac{Dq}{\alpha}\right)\overline{P}(0,s) = = -\frac{1}{2D}\exp\left[-(p+q)|x_0|\right]. \quad (26)$$

Multiplying both sides by $e^{f(s)}$, where $f'(s) = \partial f(s)/\partial s = D(p-q)/\alpha$, we can rewrite the equation as

$$e^{f(s)}\frac{\partial}{\partial s}\overline{P}(0,s) - \exp[f(s)]\left(\frac{pD}{\alpha} - \frac{Dq}{\alpha}\right)\overline{P}(0,s) = = -\frac{\exp[f(s)]}{2D}\exp[-(p+q)|x_0|]. \quad (27)$$

Using suitable integration and simple mathematics, we finally obtain

$$\overline{P}(0,s) = \frac{\exp[-f(s)]}{2D}\times \times\int_s^\infty \exp[f(s)]\exp[-(p+q)|x_0|], \quad (28)$$

where

$$f(s) = \left[\frac{-2}{2\alpha(q^2+S/D)^{3/2}} - \frac{DqS}{\alpha}\right]. \quad (29)$$

Hence, using the above equation, we are able to determine $\overline{P}(0,s)$, and once it is known we are able to determine the probability distribution function $\overline{P}(x,s)$ everywhere.

6. DETERMINATION OF THE PROBABILITY DISTRIBUTION $P(x,t)$, THE CONSTANT $a(s)$ WITH A TIME-DEPENDENT SINK TERM $k(t) = \alpha/t$

In this case, we assume that $k(t) = \alpha/t$, and hence the sink term can be written as

$$L\left[k(t)P(0,t)\right] = \int_0^\infty e^{-st}\frac{\alpha}{t}P(0,t)\,dt = = \alpha\int_s^\infty ds'\overline{P}(0,s). \quad (30)$$

We again consider Eq. (13). We hence determine the constant $a(s)$ as

$$a(s) = \frac{\omega\overline{P}(0,s)}{D\,(p+q)} + \frac{\alpha}{D\,(p+q)}\int_s^\infty ds'\overline{P}(0,s). \quad (31)$$

With this value of $a(s)$ used in Eq. (6), we obtain

$$\overline{P}(x,s) = \frac{\omega\overline{P}(0,s)\exp[-(p+q)|x|]}{D\,(p+q)} + + \frac{\alpha\exp[-(p+q)|x|]}{D\,(p+q)}\int_s^\infty ds'\overline{P}(0,s) + + \frac{\exp[-(p+q)|x-x_0|]}{2D(p+q)}. \quad (32)$$

Setting $x = 0$, after some simple modification in the above equation, we can rewrite it as

$$\overline{P}(0,s) = \frac{\alpha}{Dp}\int_s^\infty ds'\overline{P}(0,s) - \frac{\omega}{2Dp}(D+2)\overline{P}(0,s) + + \frac{1}{2Dp}\exp[-(p+q)]|x_0|]. \quad (33)$$

In solving the above equation, we consider $u(s) = \int_s^\infty ds'\overline{P}(0,s)$, and hence the above equation can be further modified as

$$\frac{du(s)}{ds} - \frac{2\alpha}{2Dp+\omega p+2\omega}u(s) = = \frac{2}{2Dp+\omega p+2\omega}\exp\left[-(p+q)|x_0|\right]. \quad (34)$$

Multiplying both sides here by $e^{f(s)}$, where $f'(s) = \partial f(s)/\partial s = 2\alpha/(2Dp+\omega p+2\omega)$, we can rewrite the equation as

$$e^{f(s)}\frac{du(s)}{ds} - e^{f(s)}\frac{2\alpha}{2Dp+\omega p+2\omega}u(s) = = \frac{2e^{f(s)}}{2Dp+\omega p+2\omega}\exp[-(p+q)|x_0|]. \quad (35)$$

Using integration and suitable mathematics for simplification, we can rewrite the above equation as

$$u(s) = e^{-f(s)}\int_s^\infty \frac{e^{f(s)}}{2Dp+\omega p+2\omega}\times \times\exp[-(p+q)|x_0|]. \quad (36)$$

With

$$f(s) = \int_0^s \frac{2\alpha\,ds}{2D(q^2+s/D)^{1/2}+2\omega+2D},$$

we can revert and calculate $\overline{P}(0,s)$ by using the expression $u(s) = \int_s^\infty ds'\overline{P}(0,s)$. Once we know $\overline{P}(0,s)$, we can calculate the probability distribution function $\overline{P}(x,s)$ everywhere.

7. SOLUTION OF THE SMOLUCHOWSKI EQUATION WITH A TIME-DEPENDENT SINK TERM $k(t) = \beta\exp(-\alpha t)$

In this case, we assume that $k(t) = \beta e^{-\alpha t}$, and hence the sink term can be written as

$$L\left[k(t)P(0,t)\right] = L\left[\beta e^{-\alpha t}P(0,t)\right] = \int_0^\infty e^{-st}\beta e^{-\alpha t}P(0,t)dt = \beta\overline{P}(0,s+\alpha). \quad (37)$$

Again using Eq. (13), we evaluate

$$a(s) = \frac{\omega}{p+q}\overline{P}(0,s) + \frac{\beta}{D(p+q)}\overline{P}(0,s+\alpha). \quad (38)$$

Substituting this value of $a(s)$ in Eq. (6), we obtain the probability distribution function as

$$\overline{P}(x,s) = \frac{\omega}{p+q}\overline{P}(0,s)\exp[-(p+q)|x|] + \frac{\beta}{D(p+q)}\overline{P}(0,s+\alpha)\exp[-(p+q)|x|] + \frac{1}{2D(p+q)}\exp[-(p+q)|x_0|]. \quad (39)$$

Setting $x = 0$ in the above equation and using some simplification, we write the above equation as

$$\overline{P}(0,s) = \frac{1}{2Dp-2\omega}\exp[-(p+q)|x_0|] + \frac{2\beta}{2Dp-2\omega}\overline{P}(0,s+\alpha). \quad (40)$$

Next to obtain a solution, we can iterate the expression to obtain the series solution

$$\overline{P}(0,s) = \sum_{n=0}^{\infty}\gamma^n\tau_n(s). \quad (41)$$

Using (41) in (40) and solving for the τ_n by equating like powers of γ, we find that

$$\tau_n(s) = \frac{1}{2D\sqrt{q^2+s/D}-2\omega}\times \exp\left[-\left(\sqrt{q^2+\frac{s}{D}}+q\right)|x_0|\right], \quad n=0,$$
$$\tau_n(s) = \prod_{j=0}^{n-1}\frac{(2)^n\exp\left[-\left(\sqrt{q^2+s/D}+q\right)|x_0|\right]}{2D\sqrt{q^2+(s+j\alpha)/D}-2\omega}, \quad n>0. \quad (42)$$

8. FIRST-ORDER RATE CONSTANT

The rate constant k can be evaluated as

$$k^{-1} = \int_0^\infty Q(t)\,dt, \quad (43)$$

where the survival probability $Q(t)$ is given by the integral

$$Q(t) = \int_{-\infty}^{\infty} P(x,t)\,dx. \quad (44)$$

Equation (43) can also be evaluated from the limit condition as

$$k^{-1} = \lim_{s\to 0}\overline{Q}(s), \quad (45)$$

where

$$\overline{Q}(s) = \int_{-\infty}^{\infty}\overline{P}(x,s) \quad (46)$$

is the Laplace transform of $Q(t)$. We note that the Laplace transform of a distribution function is sufficient for finding the first-order rate constant. Since for different time dependences of the sink term, we have different analytic expressions for the probability distribution function, the first-order rate constant can be easily calculated by using the above expressions.

9. CONCLUSIONS

We have found an exact solution for the Smoluchowski equation with a time-dependent delta function sink in many special cases. These special cases include constant, linear, inverse, and exponential time dependence. To conclude, the treatment of the time-dependent sink term is not reported until now, and we are the first to provide its analytic treatment explicitly. Further, first-order rate constant can also be calculated.

The authors want to thank IIT Mandi for a Professional Development Fund as well as an HTRA scholarship.

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